

Chem 226 Exam 2 Fall 2004: will cover Bruice, Chaps 3 through 6; Note: review e-mail & in-class quizzes and: *Worksheet (V) Introduction and Applications of Molecular Modeling:*

Conformational & Structural Exercises based on Computational Chemistry

Part I .pdf; Part II .pdf

Worksheet (VI) .pdf: Reactions of Alkenes

Optical Activity /Polarimetry: Part I & Part II

As time allows, additional practice questions for Exam 2 follow. This is an incomplete collection. Content & emphasis will vary.

1. Which of the following is not a nucleophile?

A) H_2O

B) CH_3OH

C) H_2

D) CN^-

E) NH_3

2. Which of the following species is an electrophile?

hydroxide ion

ammonia

bromine radical

bromide ion

water

3. Which statement describes the reaction coordinate diagram for an electrophilic addition reaction?

two transition states and one intermediate

one transition state and one intermediate

no transition states and one intermediate

one transition state and no intermediate

two transition states and two intermediates

4. How many transition states are there in the addition of HBr to an alkene?

0

1

2

3

4

5. How many pi bonds does an acyclic hydrocarbon with a molecular formula of $\text{C}_{20}\text{H}_{30}$ have?

5

6

7

8

10

6. What is the general molecular formula of an acyclic hydrocarbon with three double bonds?

$\text{C}_n\text{H}_{2n-5}$

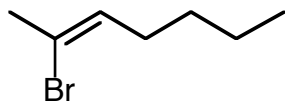
$\text{C}_n\text{H}_{2n-1}$

$\text{C}_n\text{H}_{2n-2}$

$\text{C}_n\text{H}_{2n-3}$

$\text{C}_n\text{H}_{2n-4}$

7. Name the following compound:



- Z-6-bromo-3-heptene
- E-2-bromo-4-heptene
- 6-bromo-3-heptene
- E-6-bromo-3-heptene
- Z-2-bromo-4-heptene

8. Which of the following is **not** a Z isomer?

- the isomer of 3-methyl-2-pentene with the CH₃ groups on opposite sides of the double bond
- the isomer of 3-methyl-2-pentene with the CH₃ groups on the same side of the double bond
- the isomer of 3,4-dimethyl-3-hexene with the CH₃ groups on the same side of the double bond
- the isomer of 2-pentene with the H's on the same side of the double bond
- the isomer of 2-bromo-3-methyl-2-pentene with the CH₃ groups on the same side of the double bond

9. Which statement is **not** correct?

- (Z)-4-methyl-2-pentene can be called *cis*-4-methyl-2-pentene.
- (E)-2-pentene can be called *trans*-2-pentene.
- The methyl groups in (E)-3-methyl-2-pentene are on opposite sides of the double bond.
- The methyl groups in (E)-2-methyl-2-pentene are on the same side of the double bond.
- (E)-2-butene can be called *trans*-2-butene.

10. Which relative priorities are correct?

- CH₃ < CH₂OH < CH₂NH₂ < CF₃ < CHF₂ < -CH₂F
- CH₃ < CH₂NH₂ < CH₂OH < -CH₂F < CHF₂ < CF₃
- CH₃ < CH₂OH < CH₂NH₂ < -CH₂F < CHF₂ < CF₃
- CH₂OH < CH₂NH₂ < -CH₃ < CF₃ < CHF₂ < -CH₂F
- CH₃ < CH₂NH₂ < CH₂OH < CF₃ < CHF₂ < -CH₂F

11. Which of the following could **not** be made by an electrophilic addition to a cyclohexene?

- cyclohexylbromide
- 1,2-dibromocyclohexane
- cyclohexanol
- cyclohexane
- cyclohexyl amine

12. Which of the following compounds will undergo a carbocation rearrangement when it undergoes acid-catalyzed hydration?

- 3-methyl-2-pentene
- 3-methyl-1-pentene
- 4-methyl-1-pentene
- 2-methyl-1-pentene
- 2-methyl-2-pentene

13. Which of the following carbocations is the most stable?

- (CH₃)₃C(+)
- CH₃-CH₂-CH₂-C(+)-H₂
- CH₃C(+)-H₂
- H₃C(+)
- (CH₃)₂C(+)-H

14. Which of the following is true about the transition state of an exergonic reaction?

- It will look more like the reactants.
- There is no transition state.
- It will look most like the products.
- It will be halfway between the reactants and products.

15. Two major products are formed when HBr adds to 2-cyclobutylpropene. One of them is

- 2-bromo-2-cyclobutylpropane
- 1-bromo-2-cyclopropylbutane
- 1-bromo-2-cyclobutylpropane
- 1,2-dimethyl-1-bromocyclopentane
- 2-bromo-2-cyclopropylbutane

16. Which of the following is **not** true?

- Electrophilic addition to 1-methylcyclohexene is more highly regioselective than to 4-methylcyclohexene.
- The *tert*-butyl cation is more stable than the *sec*-butyl cation.
- The isopropyl cation is more stable than the isobutyl cation.
- In an electrophilic addition reaction, the more stable carbocation is formed more slowly.
- A bromine radical is an electrophile.

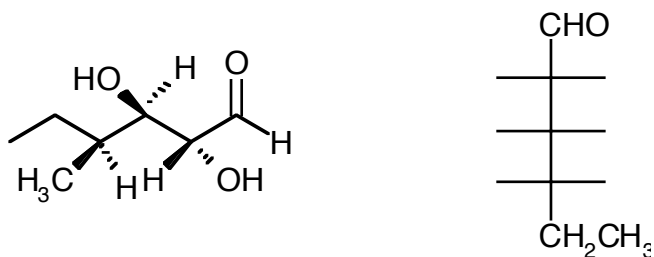
17. Which of the following reactions is regioselective?

- the reaction of 2,3-dimethyl-2-butene with HBr
- the reaction of 2-hexene with HBr
- the reaction of 1-pentene with HBr
- the reaction of 1,2-dimethylcyclohexene with HBr
- the reaction of 2-pentene with HBr

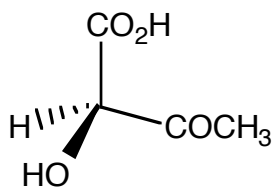
18. What is the nucleophile in the hydration of alkenes?

- Bromide ion
- Hydroxide ion
- methanol
- water
- hydronium ion

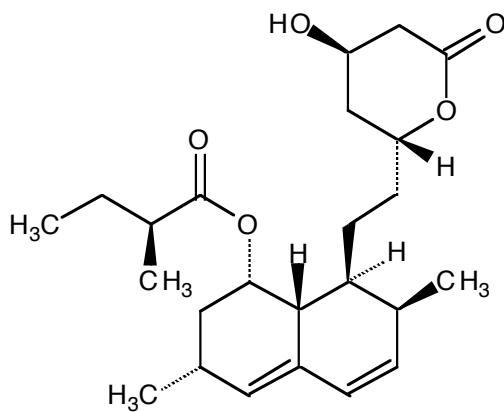
19. Complete the Fischer projection to correspond to the structure on the left.



20. Assign the (R) or (S) configuration to the following structure; label the groups 1-4 with priorities 1 > 2 > 3 > 4.



21. Circle all of the chiral carbon atoms in lovastatin, a fungal metabolite which is an antihypercholesterolemic. Its optical rotation is $[\alpha]^{25} = +323^\circ$.



How many stereoisomers are possible? _____

How many elements (degrees) of unsaturation are present? _____

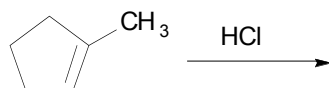
Identify two different types of functions in the molecule both of which contain oxygen.

A synthetic sample had an optical rotation of $[\alpha]^{25} = -16.25^\circ$.

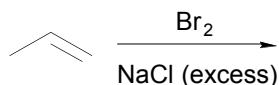
What is the optical purity (enantiomeric excess) of the sample? _____

Which isomer is in excess? (circle one): d- or l-

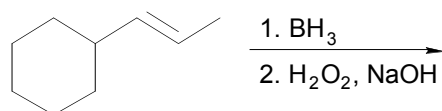
22. Give the major product(s) of the following reaction. Show stereochemistry if necessary. Is the reaction: regiospecific, regioselective, stereospecific, stereoselective, non-selective/non-specific? Circle all that apply.



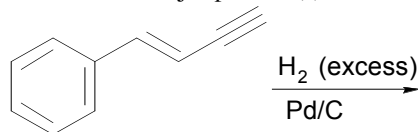
23. Give the major product(s) of the following reaction. Show stereochemistry if necessary. Is the reaction: regiospecific, regioselective, stereospecific, stereoselective, non-selective/non-specific? Circle all that apply.



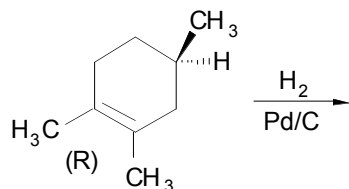
24. Give the major product(s) of the following reaction. Show stereochemistry if necessary. Show stereochemistry if necessary. Is the reaction: regiospecific, regioselective, stereospecific, stereoselective, non-selective/non-specific? Circle all that apply.



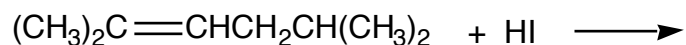
25. Give the major product(s) of the following reaction. Show stereochemistry if necessary.



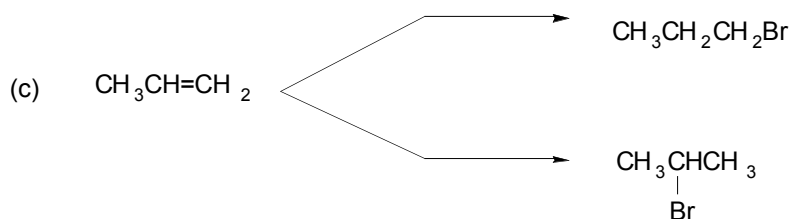
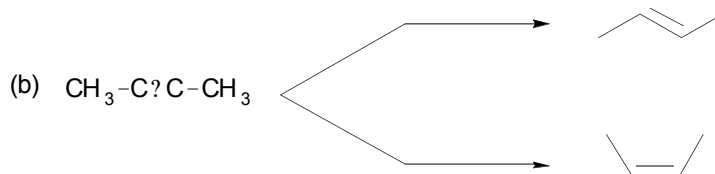
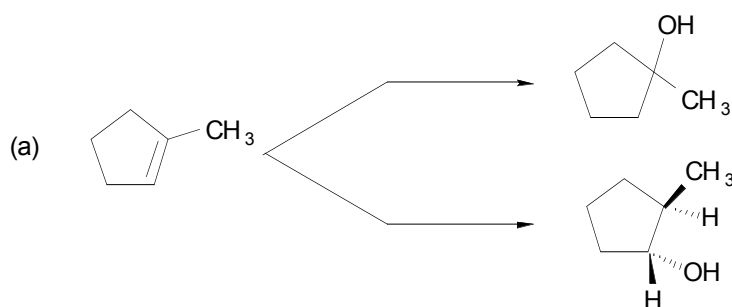
26. Bromination of Z-1-phenyl-1-propene in acetic acid at 25° gives 17% (RS, SR) and 83% (RR, SS) 1,2-dibromo-1-phenylpropane. Bromination of E-1-phenyl-1-propene under the same conditions leads to a mixture of 73% (RS, SR) and 27% (RR, SS) diastereomers of the same product. Using structures, rationalize these results in terms of mechanism and stereochemistry.
27. Give the major product(s) of the following reaction with stereochemistry where necessary and for each starting material and product indicate if it is **chiral**, **achiral** and/or **optically active**.



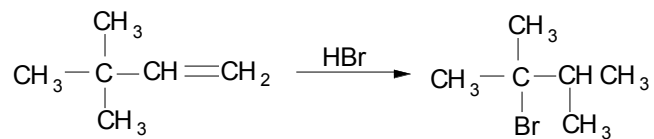
28. Suggest the major addition product that will be formed the following reaction. Is the reaction: regiospecific, regioselective, stereospecific, stereoselective, non-selective/non-specific?



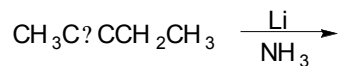
29. Account for the fact that the acid-catalyzed hydration of isobutylene (2-methylpropene) is considerably faster than the hydration of propylene under similar conditions. Use structures to illustrate your answer, and show how Hammond's Postulate is involved in your conclusion.
30. The addition of hydrogen bromide to 2-butene, hydrobromination, produces a single product with a molecular formula (C_4H_9Br). Suggest a structural formula for this product and give its IUPAC name.
31. The addition of hydrogen bromide to 1-butene leads to two different products (C_4H_9Br) depending on the reaction conditions. The isomers differ only in the position of the bromine atom. Suggest a structural formula for each product and give the IUPAC names of the products.
32. Hydration of 2-methylpropene produces exclusively 2-methyl-2-propanol. Hydration of Z-1,2-dimethylcyclohexene by water in mineral acid at 28° produces a mixture of cis-1,2-dimethylcyclohexanol (45%) and trans-1,2-dimethylcyclohexanol (55%). What do these results say about the regiospecific and stereospecific nature of the acid catalyzed hydration reaction? Be specific and use equations to illustrate your comments.
33. Selective transformations are particularly valuable in organic synthesis. Give reagents and reaction conditions for carrying out the following selective transformations.



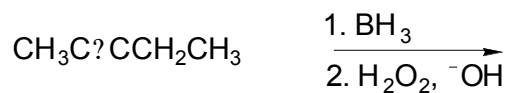
34. Draw the mechanism of the following transformation. Include all intermediates and electron-pushing arrows.



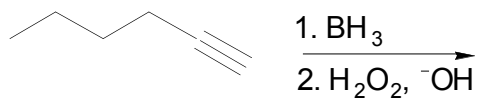
35. Give the major product(s) of the following reaction showing stereochemistry in 3-D.



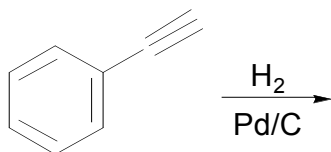
36. Give the major product(s) of the following reaction.



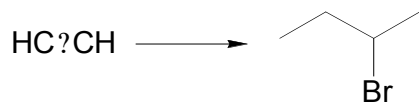
37. Give the major product(s) of the following reaction.



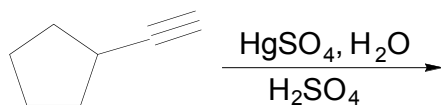
38. Give the major product(s) of the following reaction.



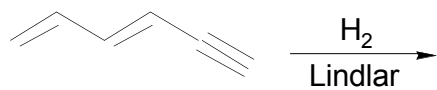
39. Show all the steps needed to accomplish the following synthesis.



40. Give the major product(s) of the following reaction.



41. Give the major product(s) of the following reaction.



42. Show all the steps needed to accomplish the following synthesis.

